

WHAT IS CLAIMED:

1. A method of preparing a shelf-stable composition which comprises:
 - a) mixing a solid thermoplastic elastomer thickener which has secondary bonding with one or more reactive liquid monomers, liquid oligomers, liquid polymers or a combination thereof which polymerizes in the presence of an activated free-radical polymerization initiator, wherein said secondary bonding comprises ionic bonding, hydrogen bonding, Van Der Waals forces, physical chain entanglements and crystal lattice interactions, wherein said solid thermoplastic elastomer thickener is free of active free-radical polymerization initiators, absorbs said reactive liquid monomers, liquid oligomers, liquid polymers or combination thereof, and reacts with said reactive liquid monomers, liquid oligomers, liquid polymers or combination thereof, in the presence of an activated free-radical polymerization initiator; and
 - b) aging the mixture of solid thermoplastic elastomer thickener, and reactive liquid monomers, liquid oligomers, liquid polymers or combination thereof, for at least 24 hours to allow absorption of the reactive liquid monomer, liquid oligomer, liquid polymer or combination thereof by the solid thermoplastic elastomer thickener.
2. A method as in claim 1, wherein long fiber reinforcement is additionally mixed with said solid thermoplastic elastomer thickener, wherein said long fiber reinforcement is insoluble in said thermoplastic elastomer thickener, has an aspect ratio, L/D, greater than 5:1 and has a length at least about 0.25mm.
3. The method as in claim 2 comprising the additional step of mixing a free-radical polymerization initiator with said mixture of solid thermoplastic elastomer thickener, reactive liquid monomers, liquid oligomers, liquid polymers or combination thereof and long fiber reinforcement wherein the free-radical polymerization initiator is inactive at ambient temperature or its activity can be restrained under ambient conditions.
4. A method as in claim 1 wherein the solid thermoplastic elastomer thickener is a thermoplastic ionomer or an acrylic block copolymer.
5. A method as in claim 1 wherein the solid thermoplastic elastomer thickener is a thermoplastic ionomer with secondary bonding comprising ionic bonds.

6. A method as in claim 5 wherein the thermoplastic ionomer comprises a polymer backbone with up to 20 mol % of carboxylate groups, sulfonate groups, phosphate groups, pyridine groups and amino groups positioned on the polymer backbone.
7. A method as in claim 6 wherein the polymer backbone is derived from free-radical polymerization of vinyl unsaturation.
8. A method as in claim 7 wherein the polymer backbone is derived from acrylate monomers, methacrylate monomers, acrylic monomers, methacrylic monomers, urethane monomers, and vinyl alcohol monomers.
9. A method as in claim 1 wherein the solid thermoplastic elastomer thickener is an acrylic polymer combined with an inorganic salt having Na^+ , Li^+ , Mg^{++} or Zn^{++} ions.
10. A method as in claim 9 wherein the acrylic polymer is polymethylmethacrylate.
11. A method as in claim 9 comprising the additional steps of heating a solid acrylic polymer to inactivate any free radical polymerization initiators therein and adding an inorganic salt to the heated acrylic polymer to form an ionomer.
12. A method as in claim 1, wherein said solid thermoplastic elastomer is a solid acrylic ionomer.
13. A method as in claim 12 which comprises a solid acrylic ionomer resin selected from the group consisting of linear homopolymers or copolymers of acrylate or methacrylate monomers.
14. A method as in claim 1, wherein the reactive liquid monomer has vinyl unsaturation and is selected from the group consisting of acrylic acid monomers, methacrylic acid monomers, acrylate monomers, methacrylate monomers, vinyl ether monomers, acrylonitrile monomers, propylene monomers, vinyl acetate monomers, vinyl alcohol monomers, vinyl chloride monomers, vinylidene chloride monomers, butadiene monomers, isobutadiene monomers, isoprene monomers, divinyl benzene and mixtures thereof and the reactive liquid oligomer is selected from acrylic oligomers, methacrylic oligomers, styrene oligomers, vinyl ester oligomers and polyester oligomers.
15. A method as in claim 1, wherein said fiber reinforcement is selected from the group consisting of glass fibers, carbon fibers, metal fibers, rayon fibers, aramid fibers and polyolefin fibers.
16. A method as in claim 1, comprising the additional step of mixing alkali earth metal filler with the solid thermoplastic elastomer thickener and one or more reactive liquid monomers, liquid oligomers, liquid pigments or combination thereof.

17. A method as in claim 2, wherein the long fiber reinforcement comprises 15 wt.% to 50 wt.% of the total composition.
18. A method as in claim 12, wherein the solid acrylic ionomer resin absorbs at least 90% of the reactive liquid monomers, liquid oligomers, liquid polymers or combination thereof, and substantial viscosity build is delayed for at least two hours after the solid acrylic ionomer resin is mixed with the reactive liquid monomer, liquid oligomer, liquid polymer or combination thereof.
19. A method as in claim 13, wherein the absorption of at least 90% of the liquid monomers, liquid oligomers, liquid polymers or combination thereof, by the solid acrylic ionomer resin is complete in 1 to 4 days from mixing the solid acrylic ionomer resin with the liquid monomer, liquid, oligomer, liquid polymer or combination thereof.
20. A composition which comprises:
 - a) a reactive liquid monomer, liquid oligomer, liquid polymer or combination thereof with vinyl unsaturation, which polymerizes in the presence of an activated free-radical polymerization initiator;
 - b) at least 1 wt.%, based on the total weight of the reactive liquid monomer, liquid oligomer, liquid polymer or combination thereof in the composition, of a solid thermoplastic elastomer thickener with secondary bonding which
 - i) is soluble in said reactive liquid monomer, liquid oligomer, liquid polymer or combination thereof, and
 - ii) reacts with the reactive liquid monomer, liquid oligomer, liquid polymer or combination thereof containing vinyl unsaturation in the presence of an activated free-radical polymerization initiator;
 - iii) is free of active free-radical polymerization initiators,
 - iv) has at least a portion of said reactive liquid monomer, liquid oligomer, liquid polymer or combination thereof absorbed therein; and
 - v) comprises a solid thermoplastic ionomer or a solid acrylic block copolymer,

c) a free-radical polymerization initiator, the activity of which can be restrained under ambient conditions or is inactive at ambient temperature so as to provide a shelf life of at least one month at ambient temperature.

21. A thermosetting molding composition as in claim 20, wherein the free-radical polymerization initiator is activated by exposure to ultraviolet light, visible light or a temperature above 75°C.

22. A composition as in claim 20, wherein the particles of solid thermoplastic elastomer thickener have an average particle size in the range of 0.005 mm (5 microns) to 0.5 mm.

23. A composition as in claim 20, wherein the amount of solid thermoplastic elastomer thickener within the molding composition is at least 35 wt.%, based on the total weight of reactive liquid monomer, liquid oligomer, liquid polymer or combination thereof in said composition.

24. A composition of claim 20 wherein the solid thermoplastic elastomer thickener is an acrylic ionomer or acrylic block copolymer.

25. A composition as in claim 24 wherein the acrylic ionomer is a linear homopolymer or copolymer of acrylate or methacrylate monomers and the acrylic block copolymer is a block copolymer of acrylate or methacrylate monomers.

26. A composition as in claim 25, wherein the reactive liquid monomer has vinyl unsaturation and is selected from the group consisting of acrylic acid monomers, methacrylic acid monomers, acrylate monomers, methacrylate monomers, vinyl ether monomers, acrylonitrile monomers, propylene monomers, vinyl acetate monomers, vinyl alcohol monomers, vinyl chloride monomers, styrene monomers vinylidene chloride monomers, butadiene monomers, isobutadiene monomers, isoprene monomers, divinyl benzene and mixtures thereof, and the reactive liquid oligomer has vinyl unsaturation and is selected from the group consisting of acrylic oligomers, methacrylic oligomers, styrene oligomers, vinyl ester oligomers, and polyester oligomers.

27. A composition as in claim 20 in the form of a bulk molding compound which additionally comprises at least 10 wt% of long fiber reinforcement which is insoluble in said solid thermoplastic elastomer thickener and has an aspect ratio (L/D) greater than 5:1 and an average length of at least 0.25 mm.

28. A composition as in claim 20 in the form of a sheet molding compound which additionally comprises at least 25 wt% of long fiber reinforcement which is insoluble in said solid thermoplastic elastomer thickener and has a length greater than 0.25 mm.

29. A composition as in claim 27 wherein said fiber reinforcement is selected from the group consisting of glass fibers, carbon fibers, metal fibers, rayon fibers, aramid fibers, and polyolefin fibers.

30. A composition as in claim 28, wherein said fiber reinforcement is selected from the group consisting of glass fibers, carbon fibers, metal fibers, rayon fibers, aramid fibers, and polyolefin fibers.

31. A composition as in claim 20, wherein at least 90% of said reactive liquid monomer, oligomer, polymer or combination thereof, is absorbed by said solid thermoplastic elastomer thickener.

32. A composition which comprises:

- a) a liquid monomer, liquid oligomer, liquid polymer or combination thereof which polymerizes in the presence of an activated free-radical polymerization initiator;
- b) a solid acrylic ionomer resin which
 - (i) is soluble in said liquid monomer, liquid oligomer, liquid polymer or combination thereof containing vinyl unsaturation,
 - (ii) has an average particle size in the range of 0.005 mm to 0.5 mm,
 - (iii) has at least a portion of said liquid monomer, liquid oligomer, liquid polymer or combination thereof containing vinyl unsaturation absorbed therein,
 - (iv) reacts with said liquid monomer, oligomer, polymer or combination thereof, and
 - (v) is free of free-radical polymerization initiators;
- c) 0.5 wt.% or more, based on the total weight of the composition, of long fiber reinforcement having an aspect ratio (L/D) greater than 5:1 and an average length of at least 0.25 mm,

wherein said composition is shelf stable for at least one month.

33. A composition as in claim 32 which is free of alkali earth metal oxide fillers.

34. A composition which comprises:

- a) a liquid monomer with vinyl unsaturation which cures to a thermoset resin in the presence of an activated free-radical polymerization initiator;
- b) at least 35 wt.%, based on the total weight of the liquid monomer in the composition, of a solid thermoplastic acrylic ionomer which is essentially free of active free-radical polymerization initiators;
- c) a free-radical polymerization initiator.

- 35. A composition as in claim 34 which additionally comprises at least 10 wt% of long fiber reinforcement having an aspect ratio (L/D) greater than 5:1.
- 36. A composition as in claim 20 which additionally comprises a solid resin, other than said solid thermoplastic elastomer thickener, which polymerizes in the presence of an activated free-radical polymerization initiator.
- 37. A composition for the preparation of dental appliances, which comprises a solid acrylic ionomer resin, a curing catalyst and long fiber reinforcement having an aspect ratio (L/D) greater than 5:1, and which has a shelf life of at least 1 week.
- 38. A composition as in claim 37, which has a shelf life of at least 1 year.
- 39. A composition as in claim 37, wherein said curing catalyst is heat activated at temperatures above 75°C and said composition remains stable at ambient temperature.
- 40. A composition as in claim 39, which is completely cured when heated to a temperature in the range of 75°C to 200°C.
- 41. A composition as in claim 40, which comprises a solid acrylic ionomer resin selected from the group consisting of monomers, oligomers and polymers of methyl methacrylate, ethyl methacrylate, vinyl ester resin and combinations thereof mixed with an inorganic salt and the amount of said solid acrylic ionomer resin is at least 10 wt.%, based on the weight of the total composition.
- 42. A composition as in claim 37, which additionally contains a liquid or solid vinyl or diene monomer, oligomer, polymer or copolymer derived from monomers selected from the group consisting of vinyl ethers, acrylonitrile, styrene, propylene, vinyl acetate, vinyl alcohol, vinyl chloride, vinyl diene chloride, butadiene, isobutylene, isoprene, divinylbenzene and mixtures thereof.
- 43. A composition for the preparation of dental appliances, which comprises a solid acrylic ionomer resin, a heat-activated curing catalyst which is stable at ambient temperature

and 2 to 90 wt.%, based on the weight of the total composition, of long fiber reinforcement having an aspect ratio (L/D) greater than 5:1 and an average length of from 0.25 mm to 6.5 mm, which has a shelf life of at least 1 week and is cured when heated to a temperature of from 75°C to 200°C.

44. A composition as in claim 43, wherein the curing catalyst is selected from the group consisting of t-butyl perbenzoate, t-butyl hydro-peroxide, peroxy ketals and Vazo 88 and said composition is essentially free of benzoyl peroxide catalyst.

45. A composition as in claim 43, which is free of alkaline earth metal oxide particulate fillers as chemical thickeners.